Motivations for ab-initio lattice dynamics I

- Vibrational spectroscopy is a sensitive probe of structure and dynamics of materials.
- All experimental methods (IR, Raman, INS, IXS) provide incomplete information.
  - IR and Raman have inactive modes
  - Hard to distinguish fundamental and overtone (multi-phonon) processes in spectra
  - No experimental technique provides complete eigenvector information ⇒ mode assignment based on similar materials, chemical intuition, guesswork.
- Hard to find accurate model potentials to describe many systems
- Fitted force-constant models only feasible for small, high symmetry systems.

Motivations from experimental spectroscopy:

IR spectrum

![IR spectrum](image)

Motivations for ab-initio lattice dynamics II

Motivations from predictive modelling

- Lattice dynamics calculation can establish stability or otherwise of putative structure.
- LD can be used to study phase transitions via soft modes.
- Quasi-harmonic lattice dynamics can include temperature and calculate ZPE and Free energy of wide range of systems.
Vibrations in Crystals

- Vibrational modes in solids take form of waves with wavevector-dependent frequencies (just like electronic energy levels).
- \( \omega(q) \) relations known as dispersion curves
- \( N \) atoms in prim. cell \( \Rightarrow 3N \) branches.
- 3 acoustic branches corresponding to sound propagation as \( q \rightarrow 0 \) and \( 3N - 3 \) optic branches.
Formal Theory of Lattice Dynamics

- Based on expansion of total energy about structural equilibrium co-ordinates

\[ E = E_0 + \sum_{\kappa,\alpha} \frac{\partial E}{\partial u_{\kappa,\alpha}} u_{\kappa,\alpha} + \frac{1}{2} \sum_{\kappa,\alpha,\kappa',\alpha'} u_{\kappa,\alpha} \Phi_{\kappa,\alpha}^{\kappa',\alpha'} u_{\kappa',\alpha'} + \ldots \]

where \( u_{\kappa,\alpha} \) is the vector of atomic displacements from equilibrium and \( \Phi_{\kappa,\alpha}^{\kappa',\alpha'} \) is the matrix of force constants

\[ \Phi_{\kappa,\alpha}^{\kappa',\alpha'} = \frac{\partial^2 E}{\partial u_{\kappa,\alpha} \partial u_{\kappa',\alpha'}} \]

- At equilibrium the forces \(- \frac{\partial E}{\partial u_{\kappa,\alpha}}\) are all zero so 1st term vanishes.

- In the Harmonic Approximation the 3rd and higher order terms are assumed to be negligible.

- Assume Born von Karman periodic boundary conditions and substituting plane-wave \( u_{\kappa,\alpha} = \epsilon_{m,\kappa,\alpha} \exp(iq_R - \omega t) \) yields eigenvalue equation:

\[ D_{\kappa,\kappa'}^{\alpha,\alpha'}(q) \epsilon_{m,\alpha} = \omega_m^2 \epsilon_{m,\alpha} \]

where the dynamical matrix

\[ D_{\kappa,\kappa'}^{\alpha,\alpha'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \Phi_{\kappa,\kappa'}^{\alpha,\alpha'}(q) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{\alpha,\beta} \Phi_{\kappa,\alpha}^{\kappa',\beta} \epsilon_{q,(R_\alpha - R_\beta)} \]

is the Fourier transform of the force constant matrix.
The Frozen-phonon method

The frozen phonon method:

- Create a structure perturbed by guessed eigenvector.
- Evaluate ground-state energy as function of amplitude \( \lambda \) with series of single-point energy calculations on perturbed configurations.
- Use \( E_0(\lambda) \) to evaluate \( k = \frac{d^2E_0}{d\lambda^2} \).
- Frequency given by \( \sqrt{k/M_{\text{rot}}} \).
- Need to use supercell commensurate with \( q \).
- Need to identify eigenvector in advance (perhaps by symmetry).
- Not a general method: useful only for small, high symmetry systems or limited circumstances otherwise.
- Need to set this up “by hand” customised for each case.

The Finite-Displacement method

The finite displacement method:

- Displace ion \( \kappa' \) in direction \( \alpha' \) by small distance \( \pm u \).
- Use single point energy calculations and evaluate forces on every ion in system \( F_{\kappa,\alpha}^+ \) and \( F_{\kappa,\alpha}^- \) for +ve and -ve displacements.
- Compute numerical derivative using central-difference formula
  \[
  \frac{dF_{\kappa,\alpha}}{du} \approx \frac{F_{\kappa,\alpha}^+ - F_{\kappa,\alpha}^-}{2u} \approx \frac{d^2E_0}{du_{\kappa,\alpha}du_{\kappa',\alpha'}}
  \]
- Have calculated entire row \( k', \alpha' \) of \( D_{\kappa,\alpha}^{\kappa',\alpha'}(q = 0) \).
- Only need \( 6N_{\text{at}} \) SPE calculations to compute entire dynamical matrix.
- This is a general method, applicable to any system.
- Can take advantage of space-group symmetry to only compute symmetry-in-equivalent perturbations.
- Like frozen-phonon method, works only at \( q = 0 \).
The Supercell method
The supercell method is an extension of the finite-displacement approach.

- Relies on short-ranged nature of FCM: $\Phi_{\alpha,\alpha'}(a) \to 0$ as $R_a \to \infty$.
- For non-polar insulators and most metals $\Phi_{\alpha,\alpha'}(a)$ decays as $1/R^3$ or faster.
- For polar insulators Coulomb term decays as $1/R^3$.
- Can define “cut off” radius $R_c$ beyond which $\Phi_{\alpha,\alpha'}(a)$ can be treated as zero.
- In supercell with $L > 2R_c$ then $C_{\alpha,\alpha'}(q = 0) = \Phi_{\alpha,\alpha'}(a)$.

Method:
1. Choose sufficiently large supercell and compute $C_{\alpha,\alpha'}(q_{\text{supercell}} = 0)$ using finite-displacement method.
2. This object is just the real-space force-constant matrix $\Phi_{\alpha,\alpha'}(a)$.
3. Fourier transform using
   \[
   D_{\alpha,\alpha'}(q) = \frac{1}{\sqrt{M_{\alpha}M_{\alpha'}}} \sum_{a,b} \Phi_{\alpha,\alpha'}(a)e^{-i\mathbf{q} \cdot (R_a - R_b)}
   \]
   to obtain dynamical matrix of primitive cell at any desired $q$.
4. Diagonalise $D_{\alpha,\alpha'}(q)$ to obtain eigenvalues and eigenvectors.

This method is often (confusingly) called the “direct” method.

First and second derivatives
Goal is to calculate the 2nd derivatives of energy to construct FCM or $D_{\alpha,\alpha'}(q)$.

- Energy $E = \langle \psi | \hat{H} | \psi \rangle$ with $\hat{H} = \nabla^2 + V_{\text{SCF}}$
- Force $F = -\frac{dE}{d\lambda} = - \left( \frac{d\psi}{d\lambda} | \hat{H} | \psi \rangle - \langle \psi | \hat{H} \frac{d\psi}{d\lambda} \right) - \langle \psi | \frac{dV}{d\lambda} | \psi \rangle$
  where $\lambda$ represents an atomic displacement perturbation.
- If $| \psi \rangle$ represents the ground state of $\hat{H}$ then the first two terms vanish because $\langle \psi | \hat{H} \frac{d\psi}{d\lambda} \rangle = \epsilon_n \langle \psi | \frac{d\psi}{d\lambda} \rangle = 0$. This is the Hellman-Feynmann Theorem.
- Force constants are the second derivatives of energy $k = \frac{d^2E}{d\lambda^2} = \left( \frac{d\psi}{d\lambda} \right| \frac{d\psi}{d\lambda} | \psi \rangle + \langle \psi | \frac{dV}{d\lambda} \right| \frac{d\psi}{d\lambda} \rangle - \langle \psi | \frac{dV}{d\lambda} | \psi \rangle$.
- None of the above terms vanishes.
- Second derivatives need linear response of wavefunctions wrt perturbation $\left( \frac{d\psi}{d\lambda} \right)$.
- In general $n$th derivatives of wavefunctions needed to compute $2n+1$th derivatives of energy. This result is the “$2n+1$ theorem”
Density-Functional Perturbation Theory

- In DFPT need first-order KS orbitals $\phi^{(1)}$, the linear response to $\lambda$.
- $\lambda$ may be a displacement of atoms with wavevector $q$ (or an electric field $E$).
- If $q$ incommensurate $\phi^{(1)}$ have Bloch-like representation: $\phi_{k,q}^{(1)}(r) = e^{-i(k+q)\cdot r}u^{(1)}(r)$ where $u^{(1)}(r)$ has periodicity of unit cell.
  ⇒ can store $u^{(1)}(r)$ in computer rep’n using basis of primitive cell.
- First-order response orbitals are solutions of Sternheimer equation

$$\begin{align*}
(H^{(0)} - \epsilon_m^{(0)})\phi_m^{(1)} &= -P_c v^{(1)}_m \\
P_c &\text{is projection operator onto unoccupied states. First-order potential } v^{(1)} \text{ includes response terms of Hartree and XC potentials and therefore depends on first-order density } n^{(1)}(r) \text{ which depends on } \phi^{(1)}. \\
\text{Finding } \phi^{(1)} \text{ is therefore a self-consistent problem just like solving the Kohn-Sham equations for the ground state.}
\end{align*}$$

- Two major approaches to finding $\phi^{(1)}$ are suited to plane-wave basis sets:

CASTEP uses Gonze’s variational DFPT method.

- DFPT has huge advantage - can calculate response to incommensurate $q$ from a calculation on primitive cell.
- Disadvantage of DFPT - lots of programming required.

Scary Maths

Second-derivatives in dynamical matrix given by:

$$
\begin{align*}
E_\epsilon^{(2)}_{s_{-q}\cdot k} &\left(u^{(0)}; u^{(1)}\right) = \frac{\Omega_0}{(2\pi)^2} \int \frac{d\epsilon}{d\lambda} \left| \nabla_q^{(1)}(1) \right|^2 \\
&\quad \left( \epsilon_m^{(0)} - \epsilon_m^{(0)} \right) \phi_m^{(1)} \\
&\quad + \frac{1}{2} \int_{k_0}^0 \frac{d^2 E_{xc}}{d\lambda d\lambda'} \left| \nabla_q^{(1)}(1) \right|^2 d\lambda + 2\pi \Omega_0 \sum_{G} \left| \nabla_q^{(1)}(G) \right|^2 \\
&\quad + \int_{k_0}^0 n^{(0)}(r) \epsilon_{\text{loc}}^{(0)}(r) dr + \frac{1}{2} \frac{d^2 E_{xc}}{d\lambda d\lambda'} \left| \nabla_q^{(1)}(1) \right|^2 \\
&\quad + 2\pi \Omega_0 \sum_{G} \left| \nabla_q^{(1)}(G) \right|^2 \\
&\quad + \frac{1}{2} \frac{d^2 E_{xc}}{d\lambda d\lambda'} \left| \nabla_q^{(1)}(1) \right|^2 \\
&\quad + 2\pi \Omega_0 \sum_{G} \left| \nabla_q^{(1)}(G) \right|^2
\end{align*}
$$
## Fourier Interpolation of dynamical Matrices

- DFPT formalism requires self-consistent iterative solution for every separate $q$.
- Hundreds of $q$’s needed for good dispersion curves, thousands for good Phonon DOS.
- Can take advantage of short-range nature of real-space FCM $\Phi^{n,n'}_{\alpha,\alpha'}(a)$.
- Compute $D^{n,n'}_{\alpha,\alpha'}(q)$ on a Monkhorst-Pack grid of $q$ vectors.
- Approximation to FCM in $p \times q \times r$ supercell given by Fourier transform of dynamical matrices on $p \times q \times r$ grid.

$$
\Phi^{n,n'}_{\alpha,\alpha'}(a) = \sum_{q} C^{n,n'}_{\alpha,\alpha'}(q) e^{i q \cdot R_a}
$$

- Fourier transform using to obtain dynamical matrix of primitive cell at any desired $q$. Exactly as with Finite-displacement-supercell method
- Diagonalise mass-weighted $D^{n,n'}_{\alpha,\alpha'}(q)$ to obtain eigenvalues and eigenvectors.
- Longer-ranged coulombic contribution varies as $1/R^3$ but can be handled analytically.
- Need only DFPT calculations on a few tens of $q$ points on grid to calculate $D^{n,n'}_{\alpha,\alpha'}(q)$ on arbitrarily dense grid (for DOS) or fine (for dispersion) path.

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## Methods in CASTEP

CASTEP can perform ab-initio lattice dynamics using

- Primitive cell finite-displacement at $q = 0$
- Supercell finite-displacement for any $q$
- DFPT at arbitrary $q$.
- DFPT on M-P grid of $q$ with Fourier interpolation to arbitrary fine set of $q$.

Full use is made of space-group symmetry to only compute only

- symmetry-independent elements of $D^{n,n'}_{\alpha,\alpha'}(q)$
- $q$-points in the irreducible Brillouin-Zone for interpolation
- electronic $k$-points adapted to symmetry of perturbation.

Limitations: DFPT currently implemented only for norm-conserving pseudopotentials and insulators. (Need fix_occupancy = T, not just band gap.)

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A CASTEP calculation I - simple DFPT

Lattice dynamics assumes atoms at mechanical equilibrium.

Golden rule: The first step of a lattice dynamics calculation is a high-precision geometry optimisation

- Parameter task = phonon selects lattice dynamics calculation.
- Iterative solver tolerance is phonon\_energy\_tol. Value of $1 \times 10^{-5}$ ev/ang$^2$ usually sufficient. Sometimes need to increase phonon\_max\_cycles
- Need very accurate ground-state as prerequisite for DFPT calculation elec\_energy\_tol needs to be roughly square of phonon\_energy\_tol
- N.B. Defaults are not very good in CASTEP 4.0. Fixed in 4.1.
- $D^{\alpha\alpha'}_{\nu\nu'}(q)$ calculated at q-points specified in cell file by one of
  - %BLOCK phonon\_kpoint\_list for the explicitly named points
  - %BLOCK phonon\_kpoint\_path to construct a path joining the nodal points given. Spacing along path is
  - phonon\_kpoint\_mp\_grid $p \ q \ r$ and possibly
  - phonon\_kpoint\_mp\_offset 0.125 0.125 0.125 to explicitly specify a M-P grid for a DOS.
  - phonon\_kpoint\_mp\_spacing $\delta q$ 1/ang to generate a M-P grid of a specified linear spacing

Example output

```
+ Vibrational Frequencies +
+ ----------------------- +
+ Performing frequency calculation at 10 wavevectors (q-pts) +
+ Branch number Frequency (cm$^{-1}$) +
+===================================================================+
+ q-pt= 1 ( 0.000000 0.000000 0.000000) 0.022727 +
+ q->0 along ( 0.050000 0.050000 0.000000) +
+------------------------------------------------------------------+
+ 1 -4.041829 0.0000000 +
+ 2 -4.041829 0.0000000 +
+ 3 -3.927913 0.0000000 +
+ 4 122.609217 7.6345830 +
+ 5 122.609217 7.6345830 +
+ 6 165.446374 0.0000000 +
+ 7 165.446374 0.0000000 +
+ 8 165.446374 0.0000000 +
+ 9 214.139992 7.6742825 +
+------------------------------------------------------------------+
```

N.B. 3 Acoustic phonon frequencies should be zero by Acoustic Sum Rule. Post-hoc correction if phonon\_sum\_rule = T.
CASTEP phonon calculations II - Fourier Interpolation

To select set phonon.fine_method = interpolate
Specify grid of \( q \)-points using phonon.kpoint_mp.grid \( p \ q \ r \).

Golden rule of interpolation: Always include the \( \Gamma \) point (0,0,0) in the interpolation grid. For even \( p, q, r \) use shifted grid
phonon.fine.kpoint_mp.offset 0.125 0.125 0.125 to shift one point to \( \Gamma \)

\( D_{\alpha \alpha'}^{\kappa \kappa'}(q) \) interpolated to \( q \)-points specified in cell file by one of

- %BLOCK phonon.fine.kpoint_list for the explicitly named points
- %BLOCK phonon.fine.kpoint_path to construct a path joining the nodal points given. Spacing along path is
  phonon.fine.kpoint_path.spacing
- phonon.fine.kpoint_mp.grid \( p \ q \ r \) and possibly
  phonon.fine.kpoint_mp.offset 0.125 0.125 0.125 to explicitly specify a M-P grid for a DOS.
- phonon.fine.kpoint_mp.spacing \( \delta q \) 1/\text{ang} to generate a M-P grid of a specified linear spacing

Real-space force-constant matrix is stored in .check file. All fine_kpoint parameters can be changed on a continuation run. Interpolation is very fast. \( \Rightarrow \) can calculate fine dispersion plot and DOS on a grid rapidly from one DFPT calculation.

Parameter phonon.force.constant_cutoff applies real-space cutoff to \( \Phi_{\alpha \alpha'}^{\kappa \kappa'}(a) \). Default is chosen according to MP grid.

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CASTEP phonon calculations III - Supercell

- To select set phonon.fine_method = supercell
  %BLOCK phonon_supercell_matrix
  2 0 0
  0 2 0
  0 0 2
  %ENDBLOCK phonon_supercell_matrix

- \( D_{\alpha \alpha'}^{\kappa \kappa'}(q) \) interpolated to \( q \)-points specified in cell file by one of same phonon.fine.kpoint keywords as for interpolation.
- Kpoints for supercell set using block or grid keywords supercell.kpoint...
- phonon.force.constant_cutoff applies as for Interpolation calculation.

Real-space force-constant matrix is stored in .check file. All fine_kpoint parameters can be changed on a continuation run. Interpolation is very fast. \( \Rightarrow \) can calculate fine dispersion plot and DOS on a grid rapidly from one DFPT calculation.

Tip. For fcc primitive cells use non-diagonal matrix
%BLOCK phonon_supercell_matrix
  1 1 -1
  1 -1 1
-1 1 1
%ENDBLOCK phonon_supercell_matrix
to make cubic supercell.

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Running a phonon calculation

- Phonon calculations can be lengthy. CASTEP saves partial calculation periodically in .check file if keywords `num_backup_iter` or `backup_interval`. Backup is every n q-vectors or every t seconds.
- Phonon calculations have high inherent parallelism. Because perturbation breaks symmetry relatively large electronic k-point sets are used.
- Number of k-points varies depending on symmetry of perturbation.
- Try to choose number of processors to make best use of k-point parallelism. If $N_k$ not known in advance choose $N_P$ to have as many different prime factors as possible - not just 2!

Convergence issues for lattice dynamics

`ab-initio` lattice dynamics calculations are very sensitive to convergence issues. A good calculation must be well converged as a function of

1. plane-wave cutoff
2. electronic kpoint sampling of the Brillouin-Zone (for crystals) (under-convergence gives poor acoustic mode dispersion as $q \to 0$
3. geometry. Co-ordinates must be well converged with forces close to zero (otherwise calculation will return imaginary frequencies.)
4. supercell size for "molecule in box" calculation and slab thickness for surface/slab calculation.

- Accuracies of 25-50 cm$^{-1}$ usually achieved or bettered with DFT.
- need GGA functional e.g. PBE, PW91 for hydrogenous and H-bonded systems.
- When comparing with experiment remember that disagreement may be due to anharmonicity.
- Less obviously agreement may also be due to anharmonicity. There is a "lucky" cancellation of anharmonic shift by PBE GGA error in OH stretch modes!
LO-TO splitting and Born effective charges

- In cubic system LO and TO mode displacements indistinguishable at $q = 0$. Nevertheless in ionic crystals LO mode freq higher than TO mode.
- Cause is additional restoring force due to macroscopic polarization.
- Lyddane-Sachs-Teller relation for cubic case: $\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\varepsilon_0}{\varepsilon_{\infty}}$
- Can calculate $\varepsilon_{\infty}$ using DFPT with $v^{(1)}$ representing electric field.
- General symmetry formalism also needs Born effective charges defined by
  \[
  Z^*_{\kappa,\beta,\alpha} = V \frac{\partial P_\beta}{\partial x_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial E_\beta}
  \]
  - $Z^*$ is polarisation per unit cell caused by displacement of atom $\kappa$ in direction $\alpha$ or force exerted on atom by macroscopic electric field.

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Electric Field response in CASTEP

- Can also apply DFPT to electric field perturbation.
- Need trick to evaluate position operator. Evaluate $\nabla_k \phi_k$. See Wannier lecture for details.
- set task = efield or task = phonon+efield
- Convergence controlled by efield_energy_tol
- Computes dielectric permittivity for crystals and polarisability (for molecules)

<table>
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<th>Optical Permittivity ($f$-&gt;infinity)</th>
<th>DC Permittivity ($f$=0)</th>
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</thead>
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<tr>
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<tr>
<td>0.00000 0.00000 3.52475 0.00000 0.00000 10.00569</td>
<td></td>
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</tbody>
</table>

Polarisabilities (Å**3)

<table>
<thead>
<tr>
<th>Optical ($f$-&gt;infinity)</th>
<th>Static ($f$=0)</th>
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</thead>
<tbody>
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<tr>
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<tr>
<td>0.00000 0.00000 5.32709 0.00000 0.00000 19.00151</td>
<td></td>
</tr>
</tbody>
</table>

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**DFPT with LO/TO splitting in NaCl**

**NaCl phonon dispersion**

![Graph showing NaCl phonon dispersion](image)

**Ionic and Electronic Dielectric Permittivity**

- Pure covalent system - Si $Z^* = -0.009$.
- Ionic system, NaCl. $\epsilon_0 = 6.95$, $\epsilon_\infty = 2.70$. $Z^*(\text{Na}) = 1.060$, $Z^*(\text{Cl}) = -1.058$
- α-quartz, SiO$_2$:
  
  \[
  \begin{array}{cccccc}
  \epsilon_\infty & 2.44 & 0.00 & 0.00 & 5.01 & 0.00 & 0.00 \\
  \epsilon_0 & 0.00 & 2.44 & 0.00 & 0.00 & 4.71 & 0.15 \\
  & 0.00 & 0.00 & 2.49 & 0.00 & 0.15 & 4.58 \\
  \end{array}
  \]

  (exp: $\epsilon_0 = 4.64/4.43$)

  \[
  Z^*(\text{O}_1) = \begin{pmatrix}
  -2.16 & -0.03 & 0.81 & 2.98 & 0.00 & 0.00 \\
  -0.08 & -1.04 & 0.14 & 2.00 & 3.67 & 0.26 \\
  0.00 & 0.00 & -1.71 & 0.00 & -0.30 & 3.45 \\
  \end{pmatrix}
  \]

- Note anisotropic tensor character of $Z^*$. 

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**QH calculations in CASTEP**

- CASTEP can evaluate Free energy:

\[
F(T) = E + k_B T \sum_k \log \left( 2 \sinh \left( \frac{\hbar \omega(k)}{2k_B T} \right) \right)
\]

- Set up phonon_fine_method = supercell or interpolation.
- .param file keyword task = thermodynamics
- Computes \(F(T)\) for range of temperatures set by parameters thermo_t_start, thermo_t_stop, thermo_t_spacing